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Photolysis of HCOOH over Rh Deposited on Pure and N-Modified TiO_2

Production of Pure H_2

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Abstract The photo-induced vapor-phase decomposition of formic acid was investigated on pure, N-doped and Rh-promoted TiO_2. The bandgap of TiO_2 was narrowed by 0.82–1.04 eV as a result of the incorporation N into TiO_2. Adsorption of formic acid on pure TiO_2 produced strong absorption bands due to formate species, the intensity of which decreased by illumination. The photodecomposition of formic acid on pure TiO_2 at 300 K occurs to only a limited extent: on N-doped TiO_2, however, it is enhanced by a factor of 2–4. The N-modified TiO_2 catalyzes the photoreaction even in the visible light, which is attributed to the prevention of electron–hole recombination. The deposition of Rh on TiO_2 markedly increased the extent of photodecomposition. The conversion is complete in 200 min, while the extent of decomposition reaches only $\sim$30% on pure TiO_2. The effect of Rh is explained by a better separation of charge carriers induced by illumination and by enhanced electron donation to the adsorbed formate species. On TiO_2 samples both the dehydrogenation and dehydration reactions occurred, on Rh/TiO_2 only a trace amount of CO was formed. Addition of water to formic acid eliminated this CO, but exerted no other influence on the occurrence the photoreaction.

Keywords Photodecomposition of formic acid · TiO_2 photocatalyst · N-doped TiO_2 · Rh-promoted TiO_2

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1 Introduction

The production of CO-free hydrogen used for fuel cell is a great challenge for catalysis. Unfortunately the decomposition of most of the oxygenated compounds, such as methanol, ethanol, dimethyl ether, produces a large amount of CO [1–3]. The level of CO can be lowered by the subsequent water–gas shift reaction, but the complete elimination of CO can not be achieved. Surprisingly formic acid as a source of hydrogen has received attention only recently [4–8]. The catalytic effect of Pt metals, Au and Mo_2C depositing on various oxides and carbon support were tested [4–8]. CO-free H_2 was obtained only on few catalysts at 423–473 K, mainly in the presence of water [4, 5, 7, 8]. In the present paper we examine the photolysis of formic acid on pure, N-doped and Rh-promoted TiO_2 with the same approach as used in the study of the photodecomposition of ethanol [9]. The primary aim is to produce H_2 virtually free of CO at ambient temperature. Although over the past decades, a tremendous amount of work has been devoted to photocatalysis (for reviews, see [10, 11]), the photoreaction of formic acid on different solids has been the subject of only relatively few studies [12–18]. The works of Medlin et al. [16, 18] deserve special attention, who studied the effect of water on the adsorption and photo-induced decomposition of formic acid using transient reaction experiments and FTIR spectroscopy. It was found that water dramatically affected the form of adsorbed formate on TiO_2.

2 Experimental

2.1 Methods

Photocatalytic reaction was followed in the same way as described in our previous paper [9]. We used a

thermostatically controllable photoreactor equipped with a 15 W germicide lamp (type GCL 307T5L/CELL, Lighttech Ltd., Hungary) as light source. This lamp emits predominantly in the wavelength range of 250–440 nm. Its maximum intensity is at 234 nm. For the visible photocatalytic experiments another type of lamp was used (Lighttech GCL 307T5L/GOLD) with 400–640 nm wavelength range and two maximum intensities at 453 and 545 nm. We note that this lamp also emits below 400 nm. The approximate light intensity at the catalyst films are 3.9 mW/cm^2 for the germicide lamp and 2.1 mW/cm^2 for the other lamp. Formic acid ($\sim$1.3%, 580 μmol) was introduced in the reactor through an externally heated tube avoiding condensation. The carrier gas was Ar, which was bubbled through formic acid at room temperature. The gas-mixture was circulated by a pump. The reaction products were analyzed with a HP 5890 gas chromatograph.

In the determination of the bandgaps of the TiO_2 samples we applied the same procedures as described in previous papers [9, 19]. The samples were pressed pellets of a mixture of 2 g of $BaSO_4$ with 50 mg of the powder. The surface area of the catalysts was determined by BET method with N_2 adsorption at $\sim$100 K. Data are listed in Table 1. For FTIR studies a mobile IR cell housed in a metal chamber was used. The cell can be evacuated to 10^{-5} Torr using a turbo molecular pumping system. The samples were illuminated by the full arc of a Hg lamp (LPS-220, PTI) outside the IR sample compartment. The IR range of the light was filtered by a quartz tube (10 cm length) filled with triply distilled water applied at the exit of the lamp. The filtered light passed through a high-purity CaF_2 window into the cell. The light of the lamp was focused onto the sample. The output produced by this setting was 300 mW cm^{-2} at a focus of 35 cm. The maximum photon energy at the sample is ca. 5.4 eV (the onset of UV intensity from the lamp). After illumination, the IR cell was moved to its regular position in the IR beam. Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument.

Table 1 Some characteristic data for pure and N-doped TiO_2

Sample	Surface area (m^2/g)	Band gap (eV)	Notation
TiO_2	200	3.17	Hombicat, as received
TiO_2 + N	96	2.35	SK, pretreatment at 673 K
TiO_2	265	3.00	SX, pretreatment at 723 K
TiO_2 + N	79	1.96	SX, pretreatment at 723 K

2.2 Materials

For the preparation of N-doped TiO_2 we applied two methods. Following the description of Beranek and Kisch [19], titania powder (Hombikat, UV 100, anatase, 200 m^2/g) was placed into 230 ml Schlenk tube connected via an adapter with 100 ml round bottom flask containing 1 g of urea and heated in a muffle oven for 30 min at 673 K. This sample is noted with "SK". In other cases TiO_2 was treated with NH_3 following the procedure of Xu et al. [20]. Titanium tetrachloride was used as a precursor. After several steps the NH_3-treated TiO_2 slurry was vacuum dried at 353 K for 12 h, followed by calcination at 723 K in flowing air for 3 h. This sample was marked "SX". TiO_2 containing 2% Rh catalysts were prepared by impregnation of pure and N-doped titania in the solution of $RhCl_3.3H_2O$. The suspension was dried at 373 K and annealed at 573 K for 1 h. For photocatalytic measurements the sample (70–80 mg) was sprayed onto the outer side of the inner tube from aqueous suspension. The surface of the catalyst film was 168 cm^2. For IR studies the dried samples were pressed in self-supporting wafers (30 × 10 mm $\sim$10 mg/cm^2). The catalysts were oxidized at 573 K and reduced at 573 K in the IR cell or in the catalytic reactor for 1 h. XPS measurements revealed that after reduction the Rh is in metallic state. The dispersity of Rh is 30.1%. The calculated average size of Rh particles is 4.3 nm. Formic acid was the product of BDH with purity of 99.5%.

3 Results

3.1 Characterization of the Samples

In the determination of bandgap energies, E_g, we followed the method and calculation procedure described by Beranek and Kisch [19]. The Kubelka–Munk function $F(R_\infty)$ vs. wavelength curves were obtained from diffuse reflectance data (Fig. 1a), and the equation $\alpha = A(h\nu - E_g)^n/h\nu$ was used in the calculation, where α is the absorption coefficient, A is a constant, $h\nu$ is the energy of light and n is a constant depending on the nature of the electron transition [21]. Assuming an indirect bandgap ($n = 2$) for TiO_2 [22] with α proportional to $F(R_\infty)$, the bandgap energy was obtained from the plots of $[F(R_\infty)h\nu]^{1/2}$ vs. $h\nu$ as the intercept at $[F(R_\infty)h\nu]^{1/2} = 0$ of the extrapolated linear part of the plot (Fig. 1b). The band gap for pure TiO_2 is 3.17 eV while that of N-modified TiO_2 is to 2.35 eV. In harmony with the elemental analysis of Beranek and Kisch [19] we found that beside N (14.9 wt%), C (7.2 wt%) has been also incorporated into TiO_2 treated at 673 K. Accordingly this C also contributes to the lowering of the band gap of TiO_2. The band gap of TiO_2 prepared by the

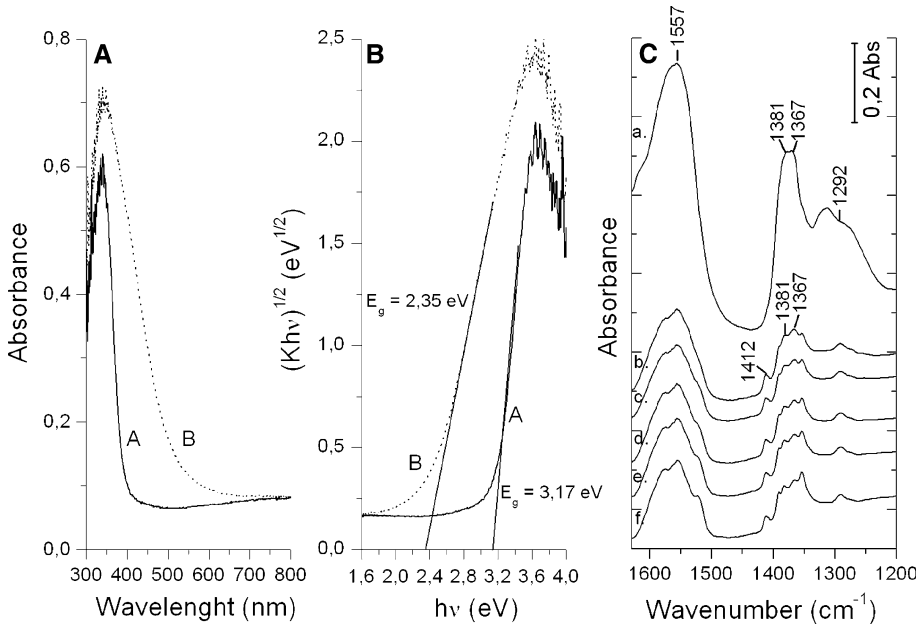

Fig. 1 Plots of Kubelka–Munk function versus wavelength of powders modified at different temperatures (a) and bandgap determination using $[F(R_\infty)h\nu]^{1/2}$ versus $h\nu$ plots (assuming indirect optical transition) for unmodified TiO_2 and TiO_2-N-modified at 673 K (SK) (b). Effects of illumination time on the FTIR spectra of adsorbed HCOOH on TiO_2 (c). Illumination time: **a** 0 min. **b** 15 min. **c** 30 min. **d** 45 min. **e** 60 min **f** 90 min

method of Xu et al. [20] was 3.0 eV, which decreased to 1.96 eV for N-doped TiO_2. Data are collected in Table 1.

3.2 In situ FTIR Measurements

Adsorption of HCOOH on pure TiO_2 produced intense absorption bands at 2,959, 2,889, 2,739, 1,557, 1,381, 1,367, and 1,292 cm^{-1}, which can be attributed to the different vibrations of formate species formed in the dissociative adsorption of formic acid. The assignment of the bands are presented in Table 2. Illumination of the adsorbed layer under continuous degassing caused a rapid initial attenuation of all the bands without any change in their position. The most important region of the IR spectra is presented in Fig. 1c. A new weak spectral feature developed at 1,412 cm^{-1} already at the beginning of irradiation, its intensity remained unaltered with the prolonged illumination. This band is very likely due to dioxymethylene [23–25] formed in the photodecomposition of formate species. The same picture was obtained on N-doped TiO_2 (SX, 573 K).

Similar FTIR spectroscopic measurements were carried out with Rh/TiO_2 samples. Adsorption of formic acid on this catalyst also gave intense formate bands. In addition, absorption features appeared in the CO stretching region at 2,054 cm^{-1} with two shoulders at 2,091 and 2,039 cm^{-1}. The 2,054 cm^{-1} can be attributed to CO linearly bonded to Rh_x, while the two shoulders to the rhodium dicarbonyl, $Rh + (CO)_2$, formed as a result of the oxidative disruption of Rh cluster induced by CO [26–28]. When the illumination was carried out in the presence of HCOOH vapor, as in the photo catalytic experiments, the intensities of these CO bands slowly increased. When the adsorbed HCOOH layer was illuminated the intensities of the formate bands at 1,557 and 1,381 cm^{-1} gradually attenuated, whereas the absorption features due to CO first increased then after certain time decreased. Addition of water to formic acid (H_2O/HCOOH ~ 1:1) markedly diminished the development and the enhancement of CO bands in the course of continuous illumination of H_2O–HCOOH vapor.

Table 2 Vibrational frequencies (in cm^{-1}) observed following the dissociative adsorption of HCOOH and their assignment

Assignment	TiO_2 [present study]	TiO_2 [18]	TiO_2 [23]
ν_a(OCO) and CH def.	2,959	2,945	2,977
ν(CH)	2,889	2,867	2,872
ν_a(OCO) + δ_a(CH)	2,739		2,754
ν_a(OCO)	1,557	1,550	1,557
ν_s(OCO)	1,381	1,378	1,386
ν_s(OCO)	1,367	1,323	1,370
CO	1,292	1,263	

3.3 Catalytic Studies

Whereas formic acid does not decompose on pure TiO_2 at 300 K, illumination induced the occurrence of the reaction. The main reaction pathway is the dehydrogenation of formic to H_2 and CO_2. CO was only the minor product. The extent of decomposition was about 15.0% in 100 min. Similar features were experienced on N-doped TiO_2 (SK). In this case CO was not produced. As the surface area of TiO_2 markedly lowered by the incorporation of N at 673 K, the data presented in Fig. 2 are related to unit surface area. Accordingly the incorporation of N into TiO_2 appreciably

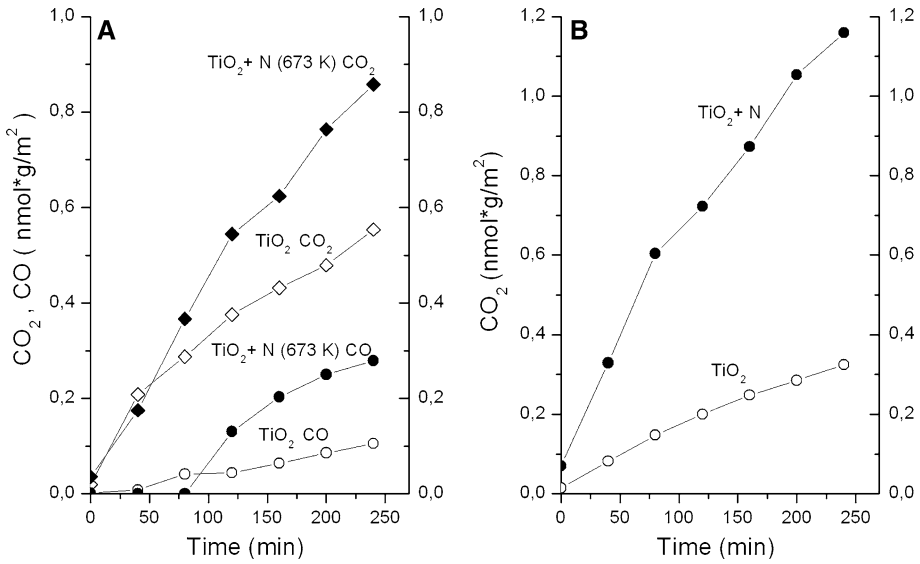

Fig. 2 Effects of illumination time on the formation of CO_2 and CO on pure and N-doped TiO_2 in the photodecomposition of HCOOH. Preparation: **a** SK, 673 K. **b** SX. In this case CO was not formed. The lamp used emits in the range of 250–440 nm

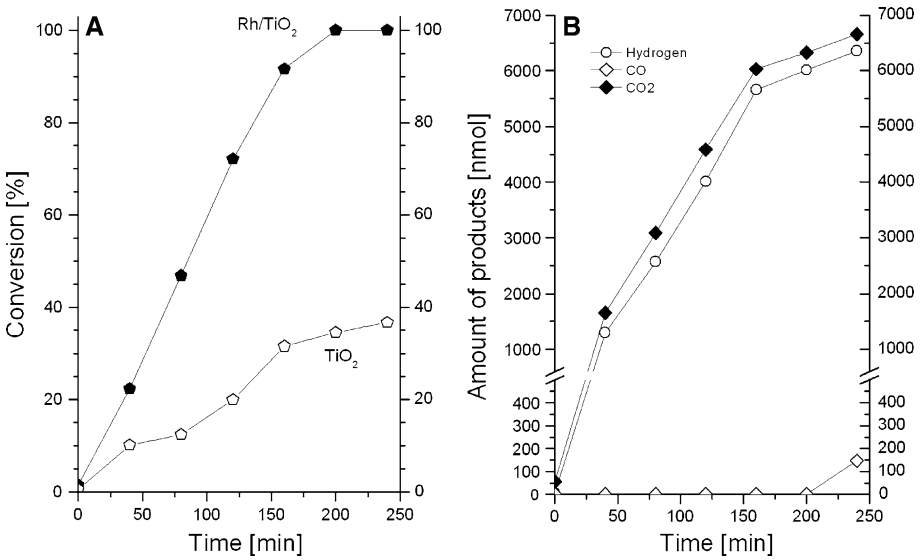

Fig. 3 Effects of illumination time on the photocatalytic decomposition of HCOOH on TiO_2 (SK) and Rh/TiO_2 (SK). **a** Conversion. **b** Formation of H_2, CO_2 and CO on Rh/TiO_2 (SK). The lamp used emits in the range of 250–440 nm

enhanced the amount of products formed in the photodecomposition. It was a general observation that the amount of H_2 was much less than that of CO_2. We experienced the same behavior in the photo-decomposition of ethanol on TiO_2 [9]. We assume that besides the reduction process a fraction of H_2 reacts with the surface species produced by the preparation of TiO_2 + N samples.

In further experiments, we examined the reaction of formic acid on 2% Rh/TiO_2 (Hombikat). The deposition of Rh on TiO_2 markedly enhanced its photoactivity. The dehydrogenation reaction remained the main reaction pathway. In this case, the amount of CO_2 agreed very well with that of H_2. In Fig. 3 we displayed the conversion of formic acid and the formation of products on various catalysts as a function of illumination time. For the demonstration of the effect of Rh the conversion of formic acid measured on pure TiO_2 is also shown in Fig. 3a. The photo-decomposition of formic acid on Rh/TiO_2 was complete in 200 min. Note that a very slight evaluation of H_2, CO_2, and CO also occurred even after formic acid has been completely reacted. This is very likely due to the decomposition of remaining formate species. When H_2O–HCOOH vapor was photolyzed the formation of CO was not detected. This is very likely the consequence of the water gas shift reaction.

Although the catalyst sample was cooled during the photolysis, the possibility cannot be excluded that the illumination caused a temperature rise of the catalyst. In order to check this possibility, a thin thermocouple was attached to the catalyst layer. The temperature rose by only a few degrees during illumination. We also examined the thermal reaction on the Rh/TiO_2 layer used for photolysis without illumination, and detected merely very slight decomposition ($\sim$1–2%) at 300 K. A measurable decomposition of

formic acid (~4% in 60 min) was observed only at 323 K. The results of these control experiments lead us to exclude the contribution of thermal effects to the decomposition of formic acid induced by photolysis.

As the narrowed bandgap of N-doped TiO_2 allows to absorb light at lower wavelengths [10, 11], measurements were also performed with the use of a lamp emitting in the visible range. These measurements were carried out with the TiO_2 samples (SX), which possesses better performance. Whereas pure TiO_2 exhibits little activity in the visible light, the photoactivity of N-doped sample (SX) is 3–4 times higher. Same feature was observed for the Rh/TiO_2 + N catalyst (SX), which also exhibited enhanced photoactivity in the visible light compared to Rh on pure TiO_2. This is illustrated in Fig. 4.

4 Discussion

Previous IR studies have clearly revealed that formic acid readily dissociates on TiO_2 to give formate species at room temperature [16, 18, 29, 30]:

$$HCOOH_{(g)} = HCOOH_{(a)} \quad (1)$$

$$HCOOH_{(a)} = HCOO_{(a)} + H_{(a)} \quad (2)$$

This process does not need illumination. Following the adsorption of HCOOH on pure TiO_2 we detected the characteristic vibration of formate bands at ~1,557 and ~1,381 cm^{-1} (Fig. 1c; Table 2). Illumination of the sample in the presence of HCOOH vapor exerted no observable change in the IR spectra. When the sample was degassed and the adsorbed layer was illuminated at 300 K, the formate bands first rapidly then slowly attenuated. This is illustrated by showing the frequency range for the asymmetric and symmetric stretching vibrations of formate (Fig. 1c). Accordingly the photolysis of the $HCOO_{(a)}$–TiO_2 system initiated the decomposition of formate on TiO_2, very probably involving the donation of a photoelectron formed in the photo-excitation process:

$$TiO_2 + h\nu = h^+ + e^- \quad (3)$$

to the formate species

$$HCOO_{(a)} + e^- = HCOO_{(a)}{}^{\delta-} \quad (4)$$

This step is followed by the photo-induced decomposition of formate to CO_2 and hydrogen:

$$HCOO_{(a)}{}^{\delta-} = CO_{2(a)}{}^{\delta-} + H_{(a)} \quad (5)$$

$$CO_{2(a)}{}^{\delta-} + h^+ = CO_{2(g)} \quad (6)$$

The small amount of CO in the products suggests that the dehydration of formic acid

$$HCOO_{(a)}{}^{\delta-} = CO_{(a)}{}^{\delta-} + OH_{(a)} \quad (7)$$

also occurs to a limited extent on TiO_2 (SK). Taking into account that the N-modified TiO_2 using two preparation methods exhibited higher photoactivity compared to that of unmodified TiO_2, we may conclude that the extent of photolysis of formic acid on TiO_2 is markedly enhanced by the narrowing of the bandgap of TiO_2. This can be attributed to the prevention of electron–hole recombination.

A considerably higher photoactivity was measured for Rh/TiO_2 catalyst. This is reflected in the conversion of formic acid, in the amounts of the products, H_2 and CO_2. The dramatic influence of Rh was also exhibited on N-doped TiO_2 in visible light. As concerns the explanation of the effect of Rh, it should be borne in mind that Rh/TiO_2 is a very active metal for the thermal decomposition of

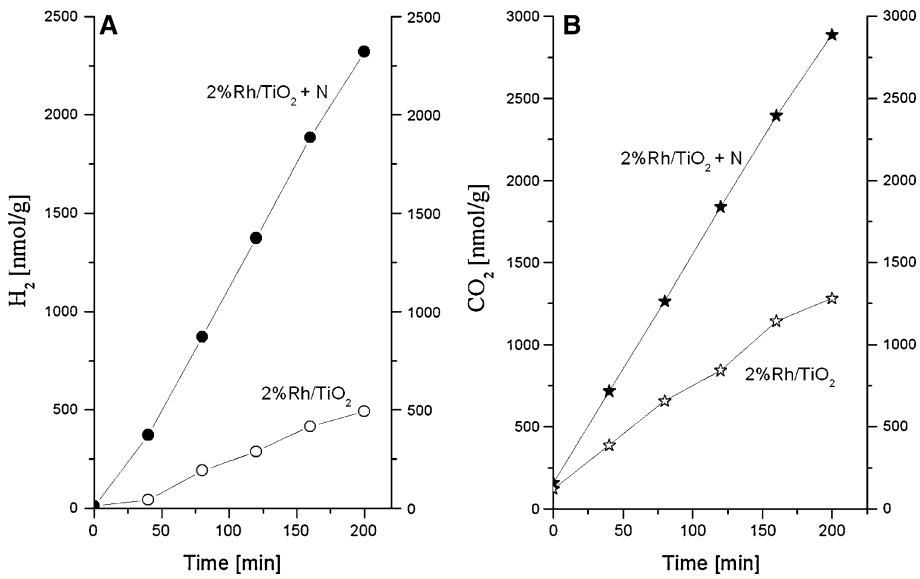

Fig. 4 Effects of N-doping of TiO_2 (SX) on the formation of products in the photocatalytic decomposition of HCOOH in the visible light over Rh/TiO_2. **a** H_2. **b** CO_2. The lamp used emits in the range of 400–640 nm

formic acid at higher temperature [29, 30]. This is attributed to facilitation of the rupture of a C–H bond in the formate species adsorbed on Rh or at Rh/TiO_2 interface.

The promoting effect of metal deposition on TiO_2 has been observed in a number of photoreactions [9–11, 16, 31–33]. This effect was explained by a better separation of charge carriers induced by illumination and by improved electronic communication between metal particles and TiO_2. We believe that the electronic interaction between the metal and *n*-type TiO_2 also plays an important role in the enhanced photoactivity of Rh/TiO_2, as demonstrated in the hydrogenation of CO_2 [34] and in the photocatalytic reaction between H_2O and CO_2 [35]. As the work function of TiO_2 ($\sim$4.6 eV) is less than that of Rh (4.98 eV), electron transfer may occur from TiO_2 to Rh, which increases the activation of CO_2 in the form of CO_2^-. The role of such electronic interaction in the activity of a supported metal catalyst was first established in the case of the decomposition of formic acid on Ni/TiO_2, when (as far as we are aware) TiO_2 was first used as a support [36]. Variation of the electron density or the work function of TiO_2 doping with altervalent cations influenced the activation energy of the decomposition of formic acid. We assume that the illumination enhances the extent of electron transfer from TiO_2 to Rh at the interface of the two solids, leading to increased decomposition. We experienced similar features in the photodecomposition of ethanol on the same TiO_2 samples [9]. However, whereas the photodecomposition of ethanol over Rh/TiO_2 gives gas mixture of H_2, CO_2, CH_4, and CO, the reforming of formic acid induced by illumination led to the formation of H_2 virtually free of CO even at room temperature.

5 Conclusions

(i) Doping TiO_2 with N greatly increased its photoactivity in the decomposition of formic acid at 300 K.
(ii) The deposition of Rh on pure or N-doped TiO_2 dramatically enhanced the extent of the photodecomposition of formic acid and in the presence of water led to the production of CO-free hydrogen.
(iii) Lowering the bandgap of TiO_2 through N incorporation facilitated the photolysis of formic acid both on TiO_2 and Rh/TiO_2 in visible light.

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